ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY, LAFAYETTE, IND.]

Hydroboration. XII. The Hydroboration of Dienes with Diborane

BY GEORGE ZWEIFEL,[1] KUNIHKO NAGASE[2] AND HERBERT C. BROWN

RECEIVED AUGUST 3, 1961

Diborane reacts with 1,3-butadiene at 0° to form a polymeric organoborane which is oxidized by alkaline hydrogen peroxide to 65–76% of 1,4- and 24–35% of 1,3-butanediol. Hydroboration of methyl substituted 1,3-dienes results in an increased preference of the boron atom for the terminal positions. Thus, 2-methyl-1,3-butadiene yields 87% of the 1,4- and only 13% of the 1,3-diol. Similarly, 2,3-dimethyl-1,3-butadiene is converted into essentially pure 2,3-dimethyl-1,4-butanediol. Hydroboration of 1,4-pentadiene yields, after oxidation, 62% of 1,4- and 38% of 1,5-pentanediol, whereas 1,5-hexadiene yields 69% of the terminal derivative, 1,6-hexanediol, with smaller quantities of the 1,5-. The high yield of the 1,4-pentanediol is attributed to an important tendency toward cyclization in the hydroboration step. 1,3-Cyclohexadiene and bicycloheptadiene were likewise converted readily into diols through this procedure. The monohydroboration of dienes was investigated by treating the diene with a controlled quantity of diborane at 0°. Monohydroboration of simple aliphatic dienes, such as 1,3-butadiene, 2-methyl-1,3-butadiene, 1,3-pentadiene and 1,4-pentadiene, occurs only to a minor extent (4–12%), with the bis-hydroboration product being formed preferentially. Under the same experimental conditions, cyclic dienes undergo monohydroboration more readily. Thus 1,3-cyclohexadiene is converted into a mixture of 2-cyclohexene-1-ol (60–65%) and 3-cyclohexene-1-ol (35–40%). Monohydroboration of bicycloheptadiene yields an 87:13 distribution of *exo*- and *endo*-dehydronorborneol.

The hydroboration of olefins, followed by oxidation with alkaline hydrogen peroxide of the intermediate organoborane, provides a convenient method for the stereospecific *cis*- and *anti*- Markownikoff hydration of double bonds.[3,4] Likewise, the hydroboration of acetylenes offers a new synthetic route for the preparation of *cis*-olefins and for the conversion of terminal acetylenes into aldehydes.[5]

It was evident that the extension of the hydroboration reaction to dienes probably would involve difficulties. First, the reaction of a polyfunctional olefin, such as a diene, with the polyfunctional diborane molecule, could result in the formation of polymers which would not exhibit the customary behavior of organoboranes. Second, conjugated dienes are less reactive toward simple addition reactions than related olefins. Consequently, the controlled monohydroboration of such dienes was a questionable possibility. However, a simple conversion of dienes into the corresponding diols or into the related unsaturated mono-ols would be a highly useful synthetic procedure. Accordingly, we undertook a study of the dihydroboration of representative dienes, as a possible synthetic route to diols, and a study of the monohydroboration of these dienes, to explore the possibility of a conversion of these derivatives into the corresponding unsaturated alcohols.[6] The results of this study are reported in the present paper. The results of a related study, utilizing disiamylborane as the hydroborating agent, are reported in the following paper.[7]

Results

Dihydroboration of 1,3-Butadiene.—In the early experiments gaseous diborane was passed into a solution of 1,3-butadiene in tetrahydrofuran at −10°.[6] Hydroboration was vigorous, but was controlled by the rate of addition of the gas. After standing at room temperature for 1–2 hours to complete the reaction, the reaction mixture was treated with water to destroy any residual hydride, followed by alkaline hydrogen peroxide. The oxidation proceeded without difficulty. The acidity of the solution was adjusted to *p*H 8 to precipitate borax (sodium tetraborate decahydrate). The liquid was decanted from the solid, tetrahydrofuran and water were removed under reduced pressure, and the residue triturated with tetrahydrofuran. After the tetrahydrofuran extract had been maintained for 24 hours at 0° to precipitate additional borax, the supernatant liquid was decanted and distilled to recover the product. An 82% yield of butanediol was realized. Gas chromatographic examination indicated the formation of 1,3- and 1,4-butanediol in a ratio of approximately 20:80.[8]

It appeared desirable to examine this reaction in considerable detail in order to establish optimum general conditions for the dihydroboration of dienes.

The isolation of the diol product in the above procedure was relatively tedious. Accordingly, we explored alternative procedures. Fortunately, it proved possible to transfer the butanediol almost quantitatively from the aqueous phase into the tetrahydrofuran phase by saturating the reaction mixture with potassium carbonate. Simple separation of the upper tetrahydrofuran solution, followed by drying over anhydrous magnesium sulfate, yielded the product in a form from which it could be isolated readily by distillation or determined by gas chromatographic analysis.

Silicone oil 200 on Haloport F or silicone–sorbitol on Chromosorb proved satisfactory for the gas chromatographic analysis of the diols.

Finally, instead of adding diborane gas to the reaction mixture, we utilized standardized solutions of diborane in tetrahydrofuran. Such solutions are readily prepared, stable over long periods of time

---

[1] Post-doctorate research associate, 1958–1959, on a grant from the Ethyl Corporation.

[2] Visiting research associate, 1960–1961.

[3] H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **78**, 5694 (1956); *J. Org. Chem.*, **22**, 1135 (1957); *J. Am. Chem. Soc.*, **81**, 6423, 6428 (1959).

[4] (a) H. C. Brown and G. Zweifel, *ibid.*, **81**, 247, 4106 (1959); (b) **82**, 4708 (1960); (c) **83**, 2544 (1961).

[5] H. C. Brown and G. Zweifel, *ibid.*, **81**, 1512 (1959); **83**, 3834 (1961).

[6] A preliminary Communication reporting the hydroboration of dienes was published earlier: H. C. Brown and G. Zweifel, *ibid.*, **81**, 5833 (1959).

[7] G. Zweifel, K. Nagase and H. C. Brown, *ibid.*, **84**, 190 (1962).

[8] These early gas chromatographic analyses for diols were relatively erratic and we were unable to rely completely on the results indicated.

TABLE I

STOICHIOMETRY OF THE REACTION OF 1,3-BUTADIENE WITH DIBORANE IN TETRAHYDROFURAN AT 0°

1,3-Butadiene, mmoles	Borane,[a] mmoles	Temp.,[b] °C.	Reaction time, hr.	Diene reacted, %	Hydrogen evolved on hydrolysis, mmoles	Yield of glycol, %	Isomer distribution, % 1,4-	1,3-	1,2-
150[c]	100	0	0.5	48					
		0	3	57					
		0	7	61					
		25	20	77					
		25	30	84					
		25	53	91	25	80[e,g]	65	31	4
100[c]	100	0	0.5	80					
		0	7	87					
		25	20	100	95	63[e,h]	66	34	
50[c]	100	0	0.5	100	172	77[e,h]	65	35	
75[d]	50	0	0.5	100	25	74[e,g]	76	21	3
200[d]	200	0	0.5	100	188	75[f,h]	76	24	

[a] Diborane exists in tetrahydrofuran solution as the borane addition compound. [b] Only rough temperature control to the nearest 5° was attempted. [c] Butadiene added to the diborane. [d] Diborane added to the butadiene. [e] Gas chromatographic analysis. [f] Isolated. [g] Analyzed on a sorbitol–silicone column. [h] Analyzed only for 1,3- and 1,4-butanediol.

when stored in a cold-room (0°),[9] and readily transferred quantitatively, at controlled rates, by means of a hypodermic syringe.

In one set of experiments, varying quantities of the diene were added to a standard quantity of diborane in tetrahydrofuran at 0°. At appropriate time intervals, samples were removed and analyzed by gas chromatography for unreacted diene, utilizing an internal standard as reference. When nearly all of the diene had reacted, a small amount of water was added to destroy residual hydride, and the organoborane was oxidized with alkaline hydrogen peroxide. After saturation with potassium carbonate, as discussed above, the dried upper layer was analyzed for diol.

In related experiments, the butadiene was first dissolved in tetrahydrofuran and the standard diborane solution added to the unsaturated hydrocarbon.

The results are summarized in Table I.

It was of interest to explore the nature of the organoborane from 1,3-butadiene and borane reacting in a ratio of 1:1. Accordingly, the product from the 1:1 reaction in tetrahydrofuran solution was treated with methanol[10] and subjected to distillation at 4 mm. pressure. However, only a negligible quantity of the total organoborane distilled under these conditions.

The results are summarized in Table II.

These results clearly point to the formation of a polymeric organoborane in the reaction.

This conclusion was further tested by carrying out the reaction of 1,3-butadiene and borane in a 1:1 ratio in a high vacuum system and then determining the molecular weight of the product in tetrahydrofuran solutoin by the lowering in vapor pressure of the solvent.[11] The molecular weight indicated was 320 to 365, nearly five times the value for the formation of a simple monomer, $(CH_2)_4BH$, indicating that the dominant reaction under these conditions is not a simple cyclization reaction.

TABLE II

METHANOLYSIS OF THE ORGANOBORANE FROM THE 1:1 REACTION OF 1,3-BUTADIENE AND BORANE

Butadiene, mmoles	Borane, mmoles	Diene reacted, %	Hydrogen evolved on methanolysis, mmoles	Distillation at 4 mm.[c] Distillate, g.	Residue g.	Boron in residue, mmoles
50[a]	50	80	65	Small amt.	4.7	47
50[b]	50	100	50	1.1	3.5	38

[a] Butadiene added to diborane at 0°. [b] Diborane added to butadiene at 0°. [c] Maximum temperature 90°.

Preparation of Diols.—Based upon the results realized in the study of 1,3-butadiene (Table I), the following procedure was selected for the dihydroboration of a number of representative dienes. A solution of diborane in tetrahydrofuran was added at 20–25° to the diene. After a short period at room temperature to complete the reaction (generally 0.5 to 2 hours), a small quantity of water was added to decompose residual hydride, followed by 3 *M* sodium hydroxide. The organoborane was then oxidized at 30–50° *in situ* by the careful dropwise addition of 30% hydrogen peroxide. The reaction mixtures then were worked up utilizing the new standard potassium carbonate technique to transfer the diol into the organic phase.

The results of these experiments are reported in Table III.

Monohydroboration of Dienes.—Early experiments had indicated that a conjugated diene is less reactive than the simple olefin in the hydroboration reaction.[6] Accordingly, it appeared desirable to make a quantitative study of the reaction of equimolar amounts of borane and representative dienes.

In these experiments 25 mmoles of the diene was added to tetrahydrofuran containing an internal standard inert toward diborane. A standard solution of diborane (4.2 mmoles of B_2H_6) in tetrahydro-

---

(9) The solutions undergo slow loss of "hydride" concentration at room temperature: J. Kollonitsch, *J. Am. Chem. Soc.*, **83**, 1515 (1961).

(10) The methanolysis of monoalkyl- and dialkylboranes had previously proven of value in establishing the formation of intermediate alkylated diboranes: H. C. Brown, A. Tsukamoto and D. B. Bigley, *J. Am. Chem. Soc.*, **82**, 4703 (1960).

(11) We are indebted to Dr. Gerald J. Klender for this experiment. Dr. Klender had earlier utilized the technique to establish that 2-methyl-2-butene reacts with diborane under the same conditions to form the simple dimeric species, tetrasiamyldiborane.

TABLE III

DIHYDROBORATION OF DIENES WITH DIBORANE—SYNTHESIS OF DIOLS

Diene	Diene, mmoles	Borane, mmoles	Reaction[a] time, hr.	Gas chromatographic analysis[b] %	diol	Product isolated, %
1,3-Butadiene	200	200	0.5[c]	24	1,3-[d]	75 (1,3- and 1,4-)
				76	1,4-[d]	
2-Methyl-1,3-butadiene	150	100	3	13	1,3-[e,d]	68 (1,3- and 1,4-)
				87	1,4-[d]	
2,3-Dimethyl-1,3-butadiene	100	100	3	100	1,4-	66 1,4-
1,4-Pentadiene	150	100	3	62	1,4-	41 1,4-
				38	1,5	
1,5-Hexadiene	150	100	3	22	1,5-[e]	
				69	1,6-	58 1,6-
				9	2,5-[e]	
1,3-Cyclohexadiene	150	100	6	Two peaks		61
Bicycloheptadiene	100	100	3	One peak		64

[a] Hydroboration at 20–25° except where otherwise indicated. [b] Of crude reaction product, before distillation, unless otherwise indicated. [c] Hydroboration at 0–5°. [d] Analysis of distilled product. [e] Assumed structure; no reference compound available.

furan was added to the diene solution at 0–5°. The reaction mixture was 0.5 *M* in diene and "hydride" (1.00 *M* B_2H_6 = 6.00 *M* "hydride"). Samples were withdrawn at one and two hours and analyzed for residual diene by gas chromatography, utilizing the internal standard as reference. Water then was added to decompose residual hydride. The hydrogen evolved was measured. The yield of the monohydroboration product was estimated from the amount of residual diene. It is evident that complete monohydroboration (100% yield) would involve the complete utilization of diene; in the case of complete dihydroboration (0% yield of monohydroboration) there would remain 12.5 mmoles of diene.

The results are summarized in Table IV.

TABLE IV

STOICHIOMETRY OF THE REACTION OF DIENES WITH DIBORANE IN AMOUNTS REQUIRED FOR MONOHYDROBORATION[a]

Diene	Residual diene, mmoles 1 hr.	2 hr.	Residual hydride, mmoles	Monohydroboration, %
1,3-Butadiene	12.5	12.0	3.7	4
2-Methyl-1,3-butadiene	12.7	12.0	2.6	4
1,3-Pentadiene	10.8	11.0	3.8	12
1,4-Pentadiene	10.2	11.2	0.2	10
1,5-Hexadiene	8.2	8.1	0.2	35
1,3-Cyclohexadiene		6.1	3.5	51
Bicycloheptadiene	8.4	8.4	0.2	34
1,5-Cycloöctadiene	12.7	11.3	0.1	10

[a] 25 mmoles of diene and 4.2 mmoles of diborane (25 mmoles of "hydride").

Preparation of Unsaturated Alcohols.—The results of the stoichiometry experiments (Table IV) indicate that the preparation of unsaturated alcohols *via* hydroboration with diborane is practical only for unconjugated aliphatic dienes. However, in cyclic systems it would appear from the results that it should be possible to stop at the monohydroboration stage both for conjugated dienes, such as 1,3-cyclohexadiene, and non-conjugated dienes, such as bicycloheptadiene. Even in these cases there is evident a competition between the two possible hydroboration stages, so that it would appear desirable to utilize an excess of the diene to favor the monohydroboration stage.

Accordingly, a solution of diborane in tetrahydrofuran was added to a 100% excess of diene at 0–5°. The reaction mixture was maintained at this temperature for 0.5 hour, and then at 20–25° for an additional 2 hours. The organoborane then was oxidized *in situ* by alkaline hydrogen peroxide in the usual manner.

The experimental results are summarized in Table V.

In the hydroboration of bicycloheptadiene with lithium borohydride and boron trifluoride etherate in ethyl ether, the yields realized were more favorable, 63% dehydronorborneol by gas chromatography and 45% of *exo*-dehydronorborneol, m.p. 92–93°, isolated.[6] We did not investigate whether this alternative hydroboration procedure was more generally effective for the monohydroboration of dienes. In part, our failure to do so was influenced by our observation that disiamylborane offers major advantages for the monohydroboration of dienes.[7]

Discussion

Dihydroboration of 1,3-Butadiene.—Our early investigations indicated that the hydroboration of 1,3-butadiene yields an intermediate organoborane which is converted *via* oxidation by alkaline hydrogen peroxide into 1,3- and 1,4-butanediol in a 20:80 ratio.[6] The hydroboration of a simple terminal olefin places the boron atom predominantly on the terminal position, 94% 1- and 6% 2-.[4b] However, in the case of styrene there is an enhanced tendency for the boron atom to add at the internal position, 80% 1- and 20% 2-, attributed to the electronic influence of the aryl substituent on the transition state.[4b] Presumably, a related influence of the vinyl substituent is responsible for the enhanced tendency of the boron atom to unite with the 2-carbon atom of the butadiene molecule.

The more intensive study of the effect of mode of addition of the diborane and of the diborane: butadiene molar ratio, summarized in Table I, reveals that the ratio of 1,3- and 1,4-butanediol formed in the reaction can be markedly influenced by the reaction conditions. Thus, the addition of the diborane to the diene in tetrahydrofuran results in a relatively rapid utilization of the available hydride, and oxidation produces a 24:76 distribution of the 1,3- and 1,4-diol. On the other hand, the reverse

Table V

Monohydroboration of Dienes with Diborane—Synthesis of Unsaturated Alcohols

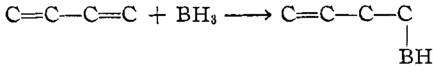
Diene	Diene, mmoles	Borane, mmoles	Isomer distribution by G. C. analysis	Product, %
1,5-Hexadiene	200	33.3	92% 5-hexene-1-ol 8% 5-hexene-2-ol[b] plus 1-hexanol	26[a]
1,3-Cyclohexadiene	200	33.3	40% 3-cyclohexene-1-ol 60% 2-cyclohexene-1-ol; sm. amt. cyclohexanol	34
Bicycloheptadiene	300	50	87% *exo*-dehydronoborneol 13% *endo*-dehydronorborneol[b]	39[a]
Bicycloheptadiene	200		88% *exo*-dehydronorborneol 12% *endo*-dehydronorborneol[b]	45[d]

[a] Based on gas chromatographic analysis. [b] Assumed structure; no reference compound available. [c] Hydroboration carried out in ethyl ether with lithium borohydride (25 mmoles = 100 mmoles "hydride") and boron trifluoride etherate. [d] Gas chromatographic analysis indicated a total yield of 63% dehydronorborneol.

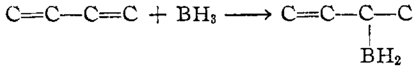
procedure, addition of the 1,3-butadiene to a solution of diborane in tetrahydrofuran, results in a hydroboration reaction which is relatively slow in the latter stages, and the amount of 1,3-diol formed increases significantly to 35%.

Our results clearly indicate that the initial hydroboration product is polymeric. Presumably the slow reaction observed in the latter stages, especially when butadiene is added to diborane, is due to the difficulties experienced by the free butadiene molecules in approaching the residual boron–hydrogen bonds entangled within the three-dimensional net-like polymer.[12]

The results of the present study suggest that the hydroboration of butadiene does not proceed through a single, simple reaction path. It is probable that the initial stage involves addition of the boron–hydrogen bond to place the boron atom primarily at the 1-position, but with nearly comparable amounts at the 2- (3 and 3′).

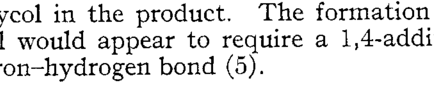


$$\mathrm{C{=}C{-}C{=}C + BH_3 \longrightarrow C{=}C{-}C{-}\underset{BH_2}{\underset{|}{C}}} \tag{3}$$

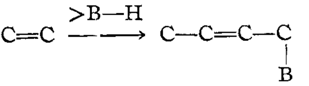


$$\mathrm{C{=}C{-}C{=}C + BH_3 \longrightarrow C{=}C{-}\underset{BH_2}{\underset{|}{C}}{-}C} \tag{3'}$$

The second stage presumably involves a second addition (4 and 4′), favored by the fact that the now isolated double bond is more reactive than the conjugated diene.

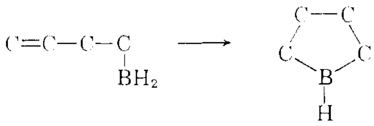


$$\mathrm{C{=}C{-}C{-}\underset{BH_2}{\underset{|}{C}} + BH_3 \longrightarrow \underset{H_2B}{\underset{|}{C}}{-}C{-}C{-}\underset{BH_2}{\underset{|}{C}}} \tag{4}$$



$$\mathrm{C{=}C{-}\underset{BH_2}{\underset{|}{C}}{-}C + BH_3 \longrightarrow \underset{H_2B}{\underset{|}{C}}{-}C{-}\underset{BH_2}{\underset{|}{C}}{-}C} \tag{4'}$$

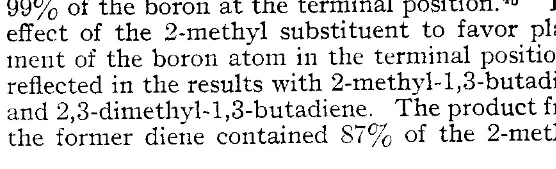
Moreover, the results with 1,4-pentadiene, described in the following section, suggest that cyclization must be an important path when the double bond is situated in position geometrically favorable for such a reaction (4′′).



(4′′)

With the boron atom possessing three hydrogen atoms capable of adding to the bifunctional butadiene molecule, this series of competing addition reactions would lead to a complex polymer with the observed properties. Oxidation would yield a mixture of 1,3- and 1,4-butanediol, as observed. Moreover, a change in the mode of addition would be expected to alter the relative importance of the different paths and bring about a change in relative amounts of 1,3- and 1,4-diols formed.

Finally, in two experiments a careful search for 1,2-butanediol indicated the presence of 3–4% of this glycol in the product. The formation of the 1,2-diol would appear to require a 1,4-addition of the boron–hydrogen bond (5).

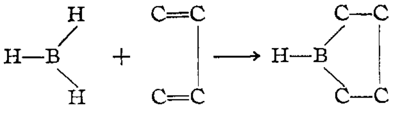


$$\mathrm{C{=}C{-}C{=}C \xrightarrow{>B-H} C{-}C{=}C{-}\underset{\substack{|\\ B\\ \wedge}}{C} \xrightarrow{>B-H} C{-}C{-}\underset{\substack{|\\ B\\ \wedge}}{C}{-}\underset{\substack{|\\ B\\ \wedge}}{C} + C{-}\underset{\substack{|\\ B\\ \wedge}}{C}{-}C{-}\underset{\substack{|\\ B\\ \wedge}}{C}} \tag{5}$$

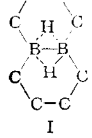
Dihydroboration of Dienes.—The hydroboration of 2-methyl-1-alkenes proceeds to place at least 99% of the boron at the terminal position.[4b] This effect of the 2-methyl substituent to favor placement of the boron atom in the terminal position is reflected in the results with 2-methyl-1,3-butadiene and 2,3-dimethyl-1,3-butadiene. The product from the former diene contained 87% of the 2-methyl-

---

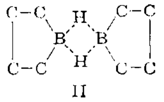
[12] Our observation that the hydroboration of 1,3-butadiene yields a polymer as the initial product appeared to be in conflict with the reports of R. Köster, *Angew. Chem.*, **71**, 520 (1959); **72**, 626 (1960). He has reported the isolation of 1,1-tetramethylene-bis-borolane, $B_2(C_4H_8)_3$, and bis-boracyclopentane, $C_4H_8BH_2BC_4H_8$, from the reaction of diborane and butadiene, and has formulated their synthesis as proceeding through the reaction of borane with butadiene through a cyclic mechanism.



However, Dr. Köster has informed the authors that these products were realized through distillation of the initial reaction products. Consequently, they appear to be redistribution products of the polymeric materials formed in the initial hydroboration stage. It should be pointed out that the unusual properties reported by Dr. Köster for "bis-boracyclopentane" are more consistent with the formulation of the structure as involving a transannular boron–hydrogen bridge (I) than with the bis-boracyclopentane formulation (II).



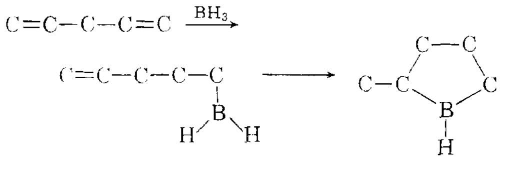
I



II

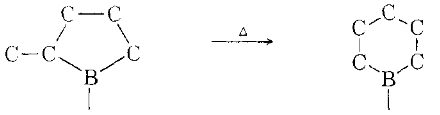
1,4-butanediol, while the latter diene yielded essentially pure 2,3-dimethyl-1,4-butanediol.

The dihydroboration of 1,4-pentadiene yielded a 62:38 distribution of 1,4- and 1,5-pentanediol. As was pointed out earlier, the hydroboration of a simple terminal olefin places 6% of the boron on the secondary position, 94% on the primary. The predominant formation of 1,4-pentanediol with its secondary alcohol group can be understood only on the basis of an *intra*-molecular addition of the second boron–hydrogen bond with the formation of a 5-membered cyclic organoborane (6).



(6)

It is noteworthy that isomerization of the bishydroboration product derived from 1,3-pentadiene yields a 6-membered cyclic organoborane[13] (7).



(7)

The glycol obtained by the oxidation of the isomerized organoborane is predominantly 1,5-pentanediol.[13] This observation argues against the thermodynamic control of the product formation in the hydroboration of dienes under our conditions.

Dihydroboration of 1,5-hexadiene, followed by oxidation, yields a mixture of diols, the main product being the 1,6-hexanediol (69%). Simple dihydroboration of 1,5-hexadiene would have been expected to yield no more than 6% of the 1,5-hexanediol. The observed formation of 22% of this product argues for the incursion of a cyclic mechanism here also. However, such a cyclic mechanism would involve a 6-membered ring, and it is apparently considerably less favorable than the 5-membered ring postulated to be one of the intermediates in the hydroboration of 1,4-pentadiene.

The dihydroboration of 1,3-cyclohexadiene and bicycloheptadiene results in the formation of a polymeric organoborane which forms a gel in the reaction mixture. The product undergoes ready oxidation to the corresponding diol or diols. However, we did not undertake structural studies of the products. Saegebarth has demonstrated the formation of *cis*-1,3-cyclopentanediol in the dihydroboration–oxidation of cyclopentadiene.[14]

Monohydroboration of Dienes.—The study of the stoichiometry of the attempted monohydroboration of dienes (Table IV) revealed that conjugated dienes, such as 1,3-butadiene, 2-methyl-1,3-butadiene and 1,3-pentadiene, undergo dihydroboration preferentially. The competitive hydroboration of a mixture of 1,3-butadiene and 1-hexene revealed the preferential hydroboration of the olefin. It appears, therefore, that conjugation stabilizes the diene toward attack by the reagent. Once monohydroboration of the diene occurs, there is present an isolated double bond in the initial hydroboration product. This isolated double bond undergoes further hydroboration in preference to the free diene.

Even in cases where the double bond is not conjugated, such as 1,4-pentadiene, preferential dihydroboration occurs. In this case, it appears that the double bond in the initial hydroboration product is ideally situated to undergo a fast second hydroboration reaction *via* a cyclic mechanism.

On a statistical basis, the monohydroboration of a diene, followed by oxidation, should yield 50% mono-ol and 25% diol. We appear to approach this statistical limit in the case of 1,5-hexadiene, although even here the results point to a significant incursion of a cyclic component to the mechanism.

Better yields of the unsaturated alcohols are realized with cyclic dienes. Thus, Winstein and his co-workers reported the isolation of a 30% yield of pure 3-cyclopentene-1-ol by the monohydroboration of cyclopentadiene.[15] The hydroboration of 1,3-cyclohexadiene provided a 34% yield of cyclohexenol. However, gas chromatographic analysis indicated the formation of two alcohols: 60–65% of 2-cyclohexene-1-ol and 35–40% of 3-cyclohexene-1-ol. It is difficult to understand the difference in the results realized with cyclopentadiene and 1,3-cyclohexadiene.

Finally, the monohydroboration of bicycloheptadiene has provided *exo*-dehydronorborneol in satisfactory yield (Table V). This procedure provides a convenient synthetic route to this compound. However, the same procedure applied to 1,5-cycloöctadiene resulted in preferential dihydroboration.

Conclusions.—This study of the reaction of diborane with dienes has opened up a number of interesting questions of both theoretical and practical importance. Thus it would be of considerable interest to understand the precise reaction path for the reaction of diborane with 1,3-butadiene and related dienes. It would be desirable to know the structure of the diol or diols formed in the dihydroboration of 1,3-cyclohexadiene, bicycloheptadiene and 1,5-cycloöctadiene. In the monohydroboration of cyclopentadiene and 1,3-cyclohexadiene, it would be of considerable interest to understand why the former yields only a single product, 3-cyclopentene-1-ol, whereas the second yields two isomeric products.

In summary, we should point out that the dihydroboration of terminal dienes with diborane proceeds simply in a number of cases and provides a satisfactory synthetic route from the diene to the α,ω-diols. Even the monohydroboration, which proceeds less simply, serves in a number of instances as a convenient route from certain dienes (cyclopentadiene, bicycloheptadiene) to the corresponding unsaturated alcohols.

Finally, we should add that additional work might have overcome some of the difficulties we encountered. We were influenced in our decision not to extend this particular phase of this study by the observation that disiamylborane circumvented a number of these difficulties and produced much

---

(13) K. A. Saegebarth, *J. Am. Chem. Soc.*, **82**, 2081 (1960).

(14) K. A. Saegebarth, *J. Org. Chem.*, **25**, 2212 (1960).

(15) E. L. Allred, J. Sonnenberg and S. Winstein, *J. Org. Chem.*, **25**, 26 (1960).

more favorable yields, both in di- and monohydroborations of dienes. The results of these studies with disiamylborane are presented in the following paper.

Experimental Part

Materials.—Tetrahydrofuran and diglyme were distilled from lithium aluminum hydride. In order to inhibit peroxidation of these solvents, 0.01% of sodium borohydride was added. Boron trifluoride ethyl etherate was treated with a small quantity of ethyl ether (to ensure an excess of this component) and distilled under reduced pressure from a few pieces of calcium hydride. Sodium borohydride from Metal Hydrides Inc. (98%) was used without purification.

The dienes were products available from commercial sources. With the exception of bicycloheptadiene and 1,5-cycloöctadiene, all of the dienes were distilled from sodium borohydride prior to their utilization. The source of the various dienes and their refractive indices are summarized in Table VI.

TABLE VI

SUMMARY OF DATA FOR THE DIENES UTILIZED

Diene	Source	$n^{20}\text{D}$	$n^{20}\text{D}$ (lit.)
1,3-Butadiene	Phillips		
2-Methyl-1,3-butadiene	Phillips	1.4225	1.4220
2,3-Dimethyl-1,3-butadiene	Columbia	1.4385	1.4392
1,3-Pentadiene (*cis-trans*)	Columbia	1.4316	
1,4-Pentadiene	Columbia	1.3890	1.3889
1,5-Hexadiene	Matheson	1.4039	1.4040
1,3-Cyclohexadiene	Farchan	1.4734	1.4736
Bicycloheptadiene	Shell	1.4707	1.4700
1,5-Cycloöctadiene	Cities Service	1.4943	1.4905 (25°)

Preparation of Diborane in Tetrahydrofuran.—In a 1-l. flask fitted with a side-arm capped by a rubber septum (t permit removal of material with a hypodermic syringe) was placed 500 ml. of tetrahydrofuran. The flask was immersed in an ice-bath. Diborane, generated by the addition of 950 ml. of a 1 *M* solution of sodium borohydride in diglyme to 1.90 moles of boron trifluoride in diglyme[16] (50% excess) and passed through a small quantity of sodium borohydride in diglyme (to remove traces of boron trifluoride which might be carried over), was dissolved in the tetrahydrofuran.

Determination of the boron and hydride by standard techniques (boron as boric acid, hydride as hydrogen gas) revealed that the solution was approximately 1.0 *M* in diborane. Stored under a nitrogen atmosphere in the cold room (0°), the concentration of the solution exhibited no measurable change over a period of several weeks.

Dihydroboration of 1,3-Butadiene.—In a 3-neck flask was placed 50 ml. of a 1.0 *M* solution of diborane in tetrahydrofuran. The flask was equipped with a thermometer, a cold trap (−78°) and an inlet for the butadiene.

1,3-Butadiene (8.1 g., 0.15 mole) was measured by volume in a cold trap at −78° (11.1 ml., d^{-78} 0.73). The diene was allowed to bubble into the diborane–tetrahydrofuran solution maintained at 0–5°. The reaction mixture was maintained at 0–5°. After several hours, the mixture was permitted to rise to 25° to hasten the completion of the reaction. At appropriate time intervals, samples were withdrawn and analyzed by gas chromatography on an adiponitrile column for residual diene. At the end of the reaction period, water was added to decompose residual hydride. The hydrogen evolved in this operation was collected and measured.

The organoborane thus produced was oxidized at 30–50° by adding 32 ml. of a 3 *M* solution of sodium hydroxide, with subsequent dropwise addition of 32 ml. of 30% hydrogen peroxide. The reaction mixture was saturated with potassium carbonate. The tetrahydrofuran layer was separated, dried over anhydrous magnesium sulfate, and analyzed by gas chromatography, with either a column of silicone oil 200 on Haloport F, or a silicon-sorbitol column on Chromosorb. 2,3-Butanediol served as internal standard.

Similar experimental conditions were utilized for the inverse addition of the reagents, except that the diborane was added to the butadiene–tetrahydrofuran solution contained in the reaction flask.

The experimental results are summarized in Table I.

Experiments Exploring the Nature of the Organoborane from the Dihydroboration of 1,3-Butadiene.—1,3-Butadiene (50 mmoles) was dissolved in 10 ml. of tetrahydrofuran and to the solution was added 25 ml. of a 1.0 *M* solution of diborane in tetrahydrofuran (50 mmoles BH_3). After 1 hour at 0°, gas chromatographic analysis of a sample indicated complete utilization of the diene. A small sample was removed—it revealed a strong infrared absorption band at 1560 cm.$^{-1}$ and a medium band at 2500 cm.$^{-1}$. To the reaction mixture at 25° was added an excess of methanol, 10 ml. Hydrogen was evolved rapidly, 50 mmoles. The tetrahydrofuran and excess methanol were removed under vacuum at room temperature, and the temperature then was raised slowly to 90° while maintaining a pressure of 4 mm. A total of 1.1 g. of distillate was obtained. There remained 3.5 g. of non-volatile residue. This was oxidized with alkaline hydrogen peroxide and analyzed for boric acid. A total of 38 mmoles, of the 50 mmoles originally introduced, was found.

Similar results were realized for an experiment where the butadiene was added to the diborane.

In a related vacuum line experiment, 1.032 mmoles of 1,3-butadiene was added to 0.503 mmole of diborane in 8.42 mmoles of tetrahydrofuran. After 2 hours the volatile components were removed, then 7.34 mmoles of ether was added. The molecular weight obtained by measuring the vapor pressure lowering of ether was 364.

Hydrolysis of the reaction mixture with water gave a 99% yield of the expected hydrogen.

Preparation of 1,4-Butanediol.—In a 500-ml. flask was placed 1,3-butadiene (10.8 g., 0.20 mole) in 200 ml. of tetrahydrofuran. The flask was immersed in an ice-bath. Diborane, 100 ml. of an approximately 1 *M* solution in tetrahydrofuran, was added slowly to the diene at 0–5°. After completion of the diborane addition, the flask was permitted to remain for 30 minutes at room temperature. The excess hydride was decomposed with water.

The organoborane was oxidized in the usual way by adding 48 ml. of 3 *M* sodium hydroxide and 48 ml. of hydrogen peroxide (30%). After remaining for 1 hour at room temperature, 150 g. of potassium carbonate was added, maintaining moderate stirring. The tetrahydrofuran layer was separated and the aqueous phase was extracted twice with 30 ml. of tetrahydrofuran. The extracts were combined, then dried over anhydrous magnesium sulfate.

The solvent was removed and the product distilled. There was obtained 13.5 g. of distillate (75% yield), b.p. 103–110° at 5 mm., $n^{20}\text{D}$ 1.4448. Gas chromatographic analysis with a column of silicone oil 200 on Haloport F indicated 24% of 1,3-butanediol and 76% 1,4-butanediol.

Preparation of 2-Methyl-1,4-butanediol.—2-Methyl-1,3-butadiene (10.2 g., 0.15 mole) was hydroborated with 50 mmoles of diborane. After oxidation and isolation as described above, there was obtained 10.7 g. of 2-methyl-1,4-butanediol (68% yield), b.p. 114–116° at 6–7 mm., $n^{20}\text{D}$ 1.4498; reported[17] b.p. 124–125° at 13 mm., $n^{18}\text{D}$ 1.4517. However, gas chromatographic analysis indicated the presence of 13% of an isomeric component, presumably 2-methyl-1,3-butanediol.

Preparation of 2,3-Dimethyl-1,4-butanediol.—2,3-Dimethyl-1,3-butadiene (8.2 g., 100 mmoles) was treated with 50 mmoles of diborane. After oxidation and isolation, there was obtained 7.8 g. of 2,3-dimethyl-1,4-butanediol (66% yield), b.p. 105–106° at 2 mm., $n^{20}\text{D}$ 1.4563. An authentic sample of 2,3-dimethyl-1,4-butanediol (*meso*) had $n^{20}\text{D}$ 1.4555.

Preparation of 1,4-Pentanediol.—1,4-Pentadiene (10.2 g., 150 mmoles) was treated with 50 mmoles of diborane, then oxidized with alkaline hydrogen peroxide. Gas chromatographic analysis of the tetrahydrofuran extract indicated 62% of 1,4-pentanediol and 38% of 1,5-pentanediol. Distillation in a Podbielniak Heligrid column yielded 6.4 g. of 1,4-pentanediol (41% yield), b.p. 221° at 753 mm., $n^{20}\text{D}$ 1.4470, bis-phenylurethan m.p. 129–131°; reported[18] $n^{20}\text{D}$ 1.4472, bis-phenylurethan m.p. 124–126°.

Preparation of 1,6-Hexanediol.—1,5-Hexadiene (12.3 g., 150 mmoles) was hydroborated and oxidized by the standard procedure. Gas chromatographic analysis of the tetra-

---

(16) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 1241 (1961).

(17) A. F. Shepard and J. R. Johnson, *J. Am. Chem. Soc.*, **54**, 4385 (1932).

(18) E. Hanschke, *Ber.*, **88**, 1048 (1955); A. Lemke and D. Tischtschenko, *Chem. Zentr.*, **110** (I), 2397 (1939).

hydrofuran extract indicated 69% 1,6-hexanediol, 22% of an isomeric component, assumed to be 1,5-hexanediol, and 9% of a third component, probably the 2,5-diol. Distillation gave 15.0 g. of product (85% yield), b.p. 104–107° at 0.6 mm. The compound crystallized on standing. Recrystallization from ethanol–ether yielded 10.2 g. of 1,6-hexanediol (58% yield), m.p. 40–43°, no depression with an authentic sample of 1,6-hexanediol.

Dihydroboration of 1,3-Cyclohexadiene.—1,3-Cyclohexadiene (12.0 g., 150 mmoles) was hydroborated with 50 mmoles of diborane. When all the diborane had been added, the reaction mixture turned into a gel. In order to obtain a homogeneous solution, the oxidation was carried out at 60–65°. Distillation of the extract resulted in 10.7 g. of product (61% yield), which solidified in the condenser. Gas chromatographic analysis indicated two peaks, tentatively identified as 1,3- and 1,4-cyclohexanediol. The existence of these in possible *cis–trans* isomeric pairs complicates the identification.

Dihydroboration of Bicycloheptadiene.—Bicycloheptadiene (9.2 g., 100 mmoles) was hydroborated with 50 mmoles of diborane. Here also a gel was produced toward the end of the diborane addition. The organoborane was oxidized at 60–65°. The tetrahydrofuran was distilled from the extract and the residue was crystallized from ether. There was obtained 8.2 g. of a crystalline product (64% yield). After recrystallization from ethanol–ether, the product, probably a bicycloheptanediol, had m.p. 183–185°.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.49. Found: C, 65.71; H, 9.59.

The mother liquor appeared to contain another compound, not further investigated. Gas chromatographic examination of the tetrahydrofuran extract with a column of silicone oil 200 on Haloport F indicated only one peak.

Monohydroboration of Dienes. Stoichiometry.—In a typical experiment, 25 ml. of a 0.166 *M* solution of diborane in tetrahydrofuran was added to 25 ml. of a 1 *M* solution of 1,3-butadiene in tetrahydrofuran containing *n*-pentane as internal standard. The diborane was added to the diene solution at 0–5° over a period of 15 minutes. Samples were withdrawn after 1 and 2 hours and quenched in 1-octene to remove residual hydride. The quenched samples were analyzed by gas chromatography on an adiponitrile column, utilizing the internal standard as reference. After 2 hours the reaction mixture was hydrolyzed with water, and the hydrogen evolved was measured.

The experimental results are summarized in Table IV.

Competitive Hydroboration of 1,3-Butadiene and 1-Hexene.—Gaseous diborane (16.6 mmoles) was passed into a solution of 1-hexene (100 mmoles) and 1,3-butadiene (100 mmoles) in tetrahydrofuran (70 ml.) at 20°. After completion of the diborane addition, the flask was permitted to remain for 1 hour at this temperature. Gas chromatographic analysis of the reaction mixture with an adiponitrile column revealed that 63% of the 1-hexene and 18% of the 1,3-butadiene had reacted.

Monohydroboration of 1,3-Cyclohexadiene.—In a 200-ml. flask was placed 1,3-cyclohexadiene (16.0 g., 200 mmoles) and 45 ml. of tetrahydrofuran. The flask was immersed in an ice-bath and 18.5 ml. of a 0.90 *M* solution of diborane in tetrahydrofuran was added slowly to the diene. The reaction mixture was maintained at 0–5° for 30 minutes, and then at room temperature for 2 hours. Water was added to decompose residual hydride. The organoborane was oxidized at 20–30° with 10.5 ml. of 3 *M* sodium hydroxide, followed by 10.5 ml. of 30% hydrogen peroxide. The reaction mixture was saturated with potassium carbonate. Distillation of the extract yielded 3.4 g. of product (34% yield), b.p. 78–80° at 20 mm., $n^{20}D$ 1.4854. Gas chromatographic analysis of the distillate on a Ucon Polar column indicated the formation of 35–40% of 3-cyclohexene-1-ol and 60–65% of 2-cyclohexene-1-ol. A sample of 3-cyclohexene-1-ol was obtained from the hydroboration of 1,4-cyclohexadiene.[7]

Preparation of *exo*-Dehydronorborneol.—Bicycloheptadiene (27.6 g., 300 mmoles) was hydroborated with 25 mmoles of diborane. Gas chromatographic analysis of the tetrahydrofuran extract indicated a 39% yield, composed of 87% *exo*- and 13% *endo*-dehydronorborneol (Ucon Polar column). The product obtained after removal of the solvent was crystallized from *n*-hexane, then sublimed. There was obtained pure *exo*-dehydronorborneol, m.p. 89–90°, phenylurethan m.p. 157–158°; reported[19] m.p. 97–99°, phenylurethan m.p. 152–154°.

In an alternative procedure, bicycloheptadiene was monohydroborated internally, by lithium borohydride and boron trifluoride etherate in ethyl ether solution.

Bicycloheptadiene (18.4 g., 200 mmoles) and 25 mmoles of lithium borohydride in 25 ml. of ether at 0° was treated with 4.6 g. (33 mmoles) of boron trifluoride etherate over 30 minutes. After 1 hour at room temperature, the ether and the excess diene were removed under vacuum. The product obtained was diluted with ether, then oxidized at 20–40° with 10.5 ml. of 3 *M* sodium hydroxide, followed by 10.5 ml. of 30% hydrogen peroxide. During the oxidation a vigorous stirring was maintained. The ether layer was separated and the aqueous phase was extracted with ether. The ether extracts were combined, then dried over anhydrous magnesium sulfate. Gas chromatographic examination indicated the formation of 63% dehydronorborneol (88% *exo*, 12% *endo*). The product obtained after removal of the solvent was crystallized from *n*-hexane at −50°. The crystalline material formed was pressed on a porous plate and yielded 4.9 g. of product (45% yield). After recrystallization and sublimation there was obtained pure *exo*-dehydronorborneol, m.p. 92–93°, phenylurethan m.p. 156–158°.

Preparation of 5-Hexene-1-ol.—1,5-Hexadiene (16.4 g., 200 mmoles) was treated with 16.6 mmoles of diborane. The usual procedure produced 2.0 g. of 5-hexene-1-ol (20% yield), b.p. 78–80° at 25 mm., $n^{20}D$ 1.4355, α-naphthylurethan m.p. 63–64°; reported[20] b.p. 152–155°, $n^{20}D$ 1.4348, α-naphthylurethan m.p. 62°.

Acknowledgment.—This investigation was made possible by funds provided by the Ethyl Corporation, and the award of a Visiting Studentship (to K. N.) from the Kao Soap Co. Ltd., Tokyo, Japan. Finally, we wish to acknowledge the invaluable assistance of Dr. Gerald J. Klender with certain of the experiments involving the hydroboration of 1,3-butadiene and the investigation of the resulting organoborane.

---

(19) J. D. Roberts, E. R. Trumbull, W. Bennett and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

(20) L. Crombie, J. Gold, S. H. Harper and B. J. Stokes, *J. Chem. Soc.*, 136 (1956).